

REMARKS

Claims 1-29 in the present application have been rejected by the Examiner based on U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Examiner cites the following as examples of indefinite language: “Relatively high molecular weight” (claims 1 and 3); “low molecular weight” (claims 1, 2, 8, 9, 10, 13, 15, 20, 23 and 25); “discrete distances” (claim 7); “small amount” (claim 8); “high mixing conditions” (claims 10 and 20); and “minor amount” (claims 13, 14, 15, 16, 23, 24, 25 and 26).

Examiner cites phrases such as “above about 200,000”, “above about 0.6” and “above about 400%” as further examples of indefinite language (see claim 1). Such phrases render the claims indefinite because, according to the Examiner, since “about” causes values slightly above and below the specified values to be encompassed, then “above about” is unclear as to whether it encompasses the specified values, as well as those slightly below.

The claim language of claims 2 and 3 is, according to the Examiner, indefinite because the phrases “the second low molecular weight diol” and “the first relatively high molecular weight diol” lack antecedent basis. Also the term “the second low molecular weight diol” is confusing because, judges the Examiner, it can be easily interpreted that there are two low molecular weight polyols.

Examiner holds that, within claim 5, the phrase “isomeric mixtures of said aliphatic or aromatic monomers” is unclear because it can refer to (1) actual mixtures of

both aliphatic and aromatic compounds or to (2) mixtures of aliphatic isomers or mixtures of aromatic isomers.

Examiner states that the ratios set forth in steps b) and e) of claim 10 are confusing because by convention one side of the ratio is unitized for clearer interpretation. Also, within step b) of claim 10, the recited ratio relates to the mole ratio of diisocyanate to prepolymer, whereas at page 9 of the specification, the ratio relates to the mole ratio of isocyanate group to hydroxyl group.

A temperature condition is not specified for the viscosity in step c) of claim 10.

The word "claim" has been omitted in claim 26 after the phrase "process of".

Examiner contends that the term "Spandex-like" in claims 11-16 and 21-26 is improper because trade names, such as Spandex, should not be used within the claims; and also because the suffix "-like" extends the scope of the term to the point where it is rendered indefinite.

Examiner rejects claim 7 and claims 10-29 under 35 U.S.C § 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention. The types of linkages encompassed by the terms "hard" and "soft" are not well-defined.

Examiner has rejected claims 1-9 under 35 U.S.C. § 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is most nearly connected, to make and/or use the invention. According to the Examiner, applicant has failed to specify the type of molecular weight (number average or weight average) for the

high molecular weight polyurethane and the relatively high molecular weight diol or how they have been determined.

Examiner has rejected claims 20-29 under 35 U.S.C. § 112, first paragraph, as containing subject matter which was not described in the specification in such a way as to enable one skilled in the art to which it pertains, or with which it is more nearly connected, to make and/or use the invention. Claim 20 and step (b) relates to a mixing of a diisocyanate and a diol at a ratio which should consume all of the diisocyanate in the reaction. However, as Examiner points out, a mixture of polymer and unreacted diisocyanate is obtained (see step (c)). How can this be?

Examiner has rejected claims 1-9, 12, 14, 16, 22, 24 and 26 under 35 U.S.C. § 102 (b) as being anticipated by Seneker, et al in U.S. Patents 5,708,118 or 5,691,441. These references disclose production of Spandex-type fibers wherein isocyanate-terminated prepolymers are chain-extended with an aliphatic amine. Also disclosed in these references are fiber compositions having high elongation and molecular weights which meet those claimed by applicant. Examiner has taken the position that applicant's claimed elongation and tenacity values are inherent properties of the fibers disclosed in the Seneker, et al. patents because said fibers are prepared from reactants equivalent to applicant's reactants and also have overlapping molecular weights. Examiner further states that no evidence has been provided to indicate that the process causes the product-by-process to have a patentable distinction.

Applicant believes that he has overcome Examiner's rejection of claims 1-29 in the present application based on U.S.C. § 112, second paragraph, as by amendment. Applicant has removed indefinite language in claim 1 by replacing the phrase "relatively

high molecular weight” with the clear and distinct phrase “a number average molecular weight of about 1,000 to about 8,000”. Support for this amendment can be found in the specification as filed at page 5, line 26. In addition, the molecular weight of the oligomeric diol (about 1,000 to about 8,000) is, of course, an average molecular weight, and is, as is customary for oligomers of this kind, a number-average molecular weight. The method of determining this number average molecular weight is based on measurement of viscosity of the oligomer in dimethylacetamide.

Applicant has removed indefinite language in claims 1, 2, 8, 9, 10, 13, 15, 20, 23 and 25 by replacing or deleting the phrase “low molecular weight”. In claim 1 the phrase “low molecular weight” has been replaced with phrase “a molecular weight of about 62 to about 118”. In claims 10 and 20 the phrase “low molecular weight” has been deleted. Support for this amendment can be found in the specification, as filed, at page 5, line 24.

In claims 8, 9, 13, 15, 23 and 25 the phrase “low molecular weight” has been amended to read “diamine which is a member selected from the group consisting of ethylene diamine; hexamethylene diamine; 1,4-diaminocyclohexane; p-phenylenediamine; 3-3' diaminodipropyl ether; diaminodibutylsulfide; and propylene diamine”. Support for this amendment can be found in the specification on page 13, line 12.

Applicant has removed the phrase “discrete distances” in claim 7 as by amendment, and believes that claim 7 is now definite and in condition for allowance. Support for the amendment can be found in the specification on page 4, line 11; and page 5, line 4.

Applicant has removed the phrase “small amount” in claim 8 as by amendment. Support for the amendment can be found in the specification on page 8, line 26; and page 9, line 5.

Applicant has amended claims 10 and 20 to remove the alleged indefinite phrase “high mixing conditions”. Support for the amendment, which includes the language “under suitable reaction conditions”, can be found in the specification on page 8, line 13.

Applicant has amended claims 13, 14, 15, 16, 23, 24, 25 and 26 to remove the alleged indefinite phrase “minor amount”. Support for the amendment, which includes the language “urea functionality”, can be found in the specification on page 8, line 27 and page 9, line 5.

The alleged indefinite language in claim 1 “above about 200,000, “above about 0.6”, and “above about 400%” has been removed by the applicant as per amendment; and replaced with clear and distinct language “about 200,000 and above”, “about 0.6 and above”, and “about 400% and above”. Applicant contends that no “new matter” has been added by the amendment, but simply that more clarity as to the nature of the invention has been added.

Claims 2 and 3 have been cancelled by applicant to remove the alleged indefinite phrases “the second low molecular weight diol” and “the first relatively high molecular weight diol”.

Applicant has amended claim 5 to remove the alleged indefinite phrase “isomeric mixtures of said aliphatic or aromatic monomers”. The amendment includes the clear and distinct language “mixtures of isomers of an aliphatic monomer having terminal isocyanate groups and mixtures of isomers of an aromatic monomer having terminal

isocyanate groups”. Applicant contends that no “new matter” has been added to the application by the amendment, but simply that more clarity has been obtained.

Applicant has amended claim 10 to more particularly point out and clearly distinguish the invention. On page 9 of the specification at line 9, an amendment has also been made to clarify the true nature of the ratio. The mole ratio of isocyanate groups (from the organic diisocyanate) to hydroxyl groups (from the polyol prepolymer) is about 2:1 to about 1:1.1. Applicant argues that no “new matter” has been added to the application because a typographical error was made to give “1:2” rather than the intended ratio of 2:1. It is further argued by applicant that a ratio of isocyanate group to hydroxyl group is identical to a ratio of diisocyanate to polyol prepolymer (when polyol refers to two and only two hydroxy groups, as is the case in the present disclosure).

Applicant has further amended claim 10 to remove the viscosity limitation in order to overcome the Examiner’s objection to the lack of a temperature condition for the specified viscosity of about 50-800 poises.

Claim 26 has been amended to include the word “claim” prior to the numeral “25”.

Applicant has amended claims 11-16 and 21-26 to remove the alleged improper claim language “Spandex-like”.

Applicant contends that the Examiner has made an error in his rejection of claim 7 and claims 10-29 under 35 U.S.C. § 112, first paragraph. On page 7 of the specification, as filed, at line 9, the types of linkages encompassed by the terms “hard” and “soft” are well-defined. On page 4 of the specification, as filed, at line 7, the relationship of the “hard” and “soft” segments along the polymeric chain is also well-defined. Also, on page

5, line 3 a well-defined description of the final product, which is a poly (ether) urethane polymer or a poly (ester) urethane polymer or a poly (ether-ester) urethane polymer, is given. The final polymer contains “an orderly arrangement” of blocks of “hard” segments and blocks of “soft” segments. On page 12, line 13, an excellent description of “soft” segments and “hard” segments is disclosed. On page 14, line 13, the importance of the “soft” segment in regulating the elongation and recovery properties of the fiber is disclosed; as well as methods of controlling the all-important length of the “soft” segment.

The prior art is replete with the commonly accepted terms of art “hard” and “soft”, as relates to the art of polyurethane chemistry. U.S. Patent Number 6,323,299 (Handlin, et al) discloses the standard urethane terminology as regards the definitions of the terms “soft” segment and “hard” segment. (Column 1, line 41). U.S. Patent Number 6,399,003 (Umezawa) discloses the use of “soft” segments and “hard” segments as relating to polyurethanes (see column 2, line 10). U.S. Patent application Publication Number 2002/0052461 (Forschner, et al) discloses the use of “soft” segments and “hard” segments when referring to polyurethane chemistry. In view of the above-cited references, applicant believes that one skilled in the art of polyurethane chemistry would be more than familiar with the terms “hard” and “soft”.

Applicant believes that Examiner’s rejection of claim 1-9 under 35 U.S.C. § 112, first paragraph is unnecessary in view of the following argument. Claims 2 and 3 have been cancelled, as by amendment. The molecular weight of the C₂ - C₆ alkylene glycol (about 62 to about 118) is based simply on atomic weights of the various elements of the monomers. As stated previously, the molecular weight of the oligomeric diol (about

1,000 to about 8,000) is of course an average molecular weight, and is, as is customary for oligomers of this kind, a number-average molecular weight. The method of determining this number average molecular weight is based on measurement of viscosity of the oligomer in dimethylacetamide.

The molecular weight of the polyurethane in claim 1 (amended) is “about 200,000 and above”. This clearly refers to the number average molecular weight because it is based on the molecular weights of typical spandex fibers, which are usually under 100,000 number average molecular weight. Some typical spandex fibers and their number average molecular weights are:

	<u>Mn</u>	<u>Mw</u>	<u>Mw/Mn</u>
Acelan	65,000	168,000	2.6
Espa T-565	84,000	262,000	3.0
Fujibo K	83,000	234,000	2.8
Gilospan	57,000	188,000	3.3
Lycra T-126	93,000	256,000	2.7
Lycra T-127	110,000	365,000	3.3

Relative viscosities of 0.5% solution of polymer in dimethylacetamide of the above-cited polymers are in the range of 0.8-1.2.

The present invention produces polymer fibers which have intrinsic viscosities of about 1.4 and above. In a preferred embodiment, the range of viscosities is from 1.8-2.4.

Polydispersity can be defined as the quotient obtained by dividing the weight average molecular weight (M_w) by the number average molecular weight (M_n).

Polydispersity of elastomeric fibers is usually in a range of about 2-6.

Applicant has amended the specification and the claims to clearly point out the fact that the molecular weights of the polyurethanes of the present invention are number average molecular weights obtained by measurements of viscosity in a flow meter.

Applicant believes that no new matter has been added to the application, as a result of these amendments, but only that more clarity as to the scope of the invention has been obtained.

Applicant believes that he has overcome Examiner's rejection of claims 20-29 under 35 U.S.C. § 112, first paragraph, by amending claim 20. Examiner is correct in asserting that all diisocyanate is used up, given the ratios recited in step (b) of claim 20. Therefore, there is no "unreacted diisocyanate" as recited in step (c) of claim 20. This deficiency has been corrected as by amendment to correctly reflect the invention as disclosed in the specification. Support for the amendment can be found on page 15, line 15 of the specification, where it is clear that more diisocyanate must be added, given the ratios recited in step (b) of claim 20.

Applicant contends that Examiner's rejection of claims 1-9, 12, 14, 16, 22, 24 and 26 under 35 U.S.C § 102 (b) as being anticipated by Seneker, et al in U.S. Patents 5,708,118 or 5,691,441 is unwarranted. The Seneker, et al 5,708,118 and 5,691,441 patents relate to poly (urea) urethane compositions which do not melt, and hence are not melt-spinnable. They must be spun from solvents. In the present inventive disclosure, a solventless melt spinning process is employed to obtain polyurethane fibers. Also, the

Seneker, et al patents disclose processes for preparing poly (urea) urethane compositions which are composed of randomly spaced "hard" segments and "soft" segments. This is because the "hard" segments and "soft" segments are not prepared separately.

Applicant's invention relates to a process for preparing the "hard" segments and "soft" segments separately, thus giving rise to a polymer product having properties distinguishable over Seneker, et al.

CONCLUSION

A substitute specification has been submitted in accordance with 37 CFR § 1.125. Claims 2 and 3 have been cancelled and claims 1, 5, 7-16, 20-26, and 29 have been amended. There are 3 independent claims and 27 total claims now pending in the application. The original filing fee covers the claims now pending. Applicant respectfully requests reconsideration of the present application, as amended, and asks that the Examiner hold that the present application is now in condition for allowance.

Respectfully submitted,

A handwritten signature in black ink that reads "Leander F. Aulisio". The signature is written in a cursive, flowing style.

Leander F. Aulisio
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MARKED UP COPY OF SUBSTITUTE SPECIFICATION

Field of the Invention

5 The present invention relates generally to the preparation of melt spinnable thermoplastic polyurethane elastomers and, more specifically, to the preparation of polyurethane elastomers utilizing a novel multi-step polymerization process.

Background of the Invention

10 Melt-spun elastomeric fibers have been in the past unacceptable for use as textile fibers because they have very low tenacity and poor recovery from elongation. Also, melt-spinnable thermoplastic urethane polymers have in the past formed gels too readily, thus inhibiting spinning of the material.

15 Prior art methods of forming melt-spun polyurethane fibers include the use of a "one shot process" wherein mixtures of diisocyanates, a polymeric glycol "soft" segment, and a low molecular weight glycol and a catalyst are all added to an extruder with mixing at a temperature of about 100°C to about 250°C and a time of about 1-5 minutes to obtain, after spinning,
20 a polyurethane fiber. The properties of this fiber are limited because of the randomness of the polymerization process, the required rapid reaction and the substantially poor mixing. The urethane groups in the final product have no orderly arrangement, causing poor tenacity, unacceptable recovery from
25 elongation and an unacceptable

amount of gel formation.

The preparation of plastics in extruders is generally known. In contrast to the processing of plastics by a purely thermoplastic method, the term “reaction extrusion” is used in the case of such polymer synthesis in an extruder. Accordingly, the extruder used as the chemical reactor is frequently also referred to as a “reaction extruder”.

Almost without exception, the literature recommends the twin-screw extruder in which both screws rotate in the same direction, for the synthesis of polyurethanes. Single-screw extruders and twin-screw extruders having counter-rotating screws are unsatisfactory owing to the poor mixing effect during passage through the extruder, and extruders having more than two screws are too expensive.

U.S. Patent No. 5,621,024 (Eberhardt, et al) discloses a process for preparing thermoplastic polyurethane employing a twin-screw extruder having multiple zones. All reactants are fed as a low viscosity mixture to the extruder in a “one shot” process.

U.S. Patent No. 5,136,010 (Reisch, et al) discloses a method of preparing a cast polyurethane or polyurea elastomer. The method comprises the steps of : fabricating a polyol having a specified molecular weight, reacting the polyol with a polyisocyanate to obtain an isocyanate-terminated prepolymer, and reacting the prepolymer with a non- (ethylene glycol) chain extender. The elastomer is prepared in a “one shot” process.

U.S. Patent No. 5,116,931 (Reisch, et al) discloses a thermoset polyurethane or polyurea elastomer prepared in a “one shot” process.

5 U.S. Patent No. 5,096,993 (Smith, et al) discloses a thermoplastic polyurethane or polyurea elastomer made by reacting in a “one shot” process a polyether diol, diisocyanate[,] and a chain extender. The [Chain] chain extender is a difunctional, isocyanate-reactive material.

10 U.S. Patent No. 3,233,025 (Frye, et al) discloses a method of forming a thermoplastic polyurethane having free isocyanate groups. The method comprises the steps of mixing reactive components comprising an excess of an organic polyisocyanate and an organic compound containing at least
15 two active hydrogen containing groups, reacting in a passageway at a temperature of about 60°C to about 250°C and a limited residence time, and removing the thermoplastic polyurethane. A twin-screw extruder can be employed.

20 Summary of the Invention

In one aspect, the present invention relates to a melt spinnable thermoplastic polyurethane elastomeric polymer made by a three-step process. Fibers prepared from the polyurethane elastomer have a tenacity [above] of about 0.6gm/denier and
25 above, an elongation [above] of about 400% and above, a percentage set from 200% stretch [below] to about 10%, and gels of [below] about 1 ppm and below in the melt. An

advantage of the melt spinning is the ability to make a large range of sizes, all of which can be round, which is in contrast to the dry spinning processes.

5 The polyurethane fiber of the present disclosure exhibits unique structural properties on the molecular level. These properties allow the fiber to imitate the physical properties of well-known poly(ester)urea urethanes or poly(ether)urea urethanes such as Lycra®Spandex. The molecular structure of the fibers of the present disclosure reveals relatively similar
10 lengths of “soft” segments spaced at substantially equal distance (by relatively similar lengths of “hard” segments) along the polymeric chain. The resulting configuration is an orderly arrangement of blocks of “hard” segments and blocks of “soft” segments. The orderly arrangement, unachievable in a
15 conventional “one shot” process, gives the polyurethane fiber the qualities of high tenacity, high elongation and low set.

The molecular polarity of the polyurethane fiber of the present disclosure is weaker than the polarity of the Lycra®Spandex molecules because of a substantial lack of urea
20 functionality in the polyurethane molecules. In order to compensate for this diversity in polarity, the present polyurethane fiber has a substantially higher molecular weight than Lycra®Spandex molecules.

25 A process for preparing a melt spinnable elastomeric polyurethane polymer is disclosed. The process comprises the steps of : preparing a first poly(ether)urethane oligomer (or

poly(ester)urethane oligomer); preparing a second poly(C₂-C₆ glycol)urethane oligomer; and reacting in a reaction extruder, under relatively high mixing conditions, the first “soft” oligomer and the second “hard” oligomer. The final product is a poly(ether)urethane polymer or a poly(ester)urethane polymer containing an orderly arrangement of blocks of “hard” segments and blocks of “soft” segments. The term “polyurethane polymer” includes poly(ether)urethane polymer, poly(ester)urethane polymer, and poly(ether-ester)urethane polymer. These and other aspects of the invention will become apparent upon reading the following detailed description of the invention.

Detailed Description of the Invention

The present disclosure relates to a melt spinnable composition useful in preparing textile fibers. The composition comprises a high molecular weight polyurethane polymer prepared from conventional starting materials. The polymer is prepared from at least two diol monomers wherein the two diol monomers are always reacted separately, and never in a “one shot” process.

The two diol monomers, which are always to be reacted separately, are: a first diol monomer of relatively high molecular weight and a second diol monomer of low molecular weight. The second diol monomer preferably has terminal hydroxyl groups, and has a molecular weight of about 62 to 122. The first diol monomer preferably has terminal hydroxyl

groups, and has a number average molecular weight of about 1,000 to about 8,000. In a preferred embodiment, the first diol monomer is a member selected from the group consisting of a polyether diol, a polyester diol and a mixed polyether-polyester diol.

The separate reactions of the two diol monomers are conducted in both cases with a diisocyanate monomer reactant. In a preferred embodiment, the diisocyanate monomer reactant is the same in both cases. Included within this preferred embodiment is the process wherein the same mixture of two or more diisocyanate monomers is employed.

The diisocyanate monomer preferably has terminal isocyanate groups, and the diisocyanate can be aliphatic or aromatic. Isomeric mixtures of diisocyanates can also be employed. Examples of diisocyanate monomers are 1, 6-hexane diisocyanate, all isomers of toluene diisocyanate, and methylene diisocyanate.

The reaction between the second low molecular weight diol and the diisocyanate yields a product that is solid and potentially hard to melt. The length of the polymer chain which is prepared from the low molecular weight diol must be carefully controlled. Otherwise, the "hard segment", prepared from the low molecular weight diol and a diisocyanate, becomes intractable during the melt spinning process.

After the separate reactions of the two diol monomers are conducted, the two products are worked up and purified, if desired. When these two products are combined under reaction

conditions in a reaction extruder along with suitable catalyst, a final polyurethane polymer product is obtained. The polyurethane polymer has a number average molecular weight of about 100,000 and above, and preferably about 200,000 and above. The tenacity of the polymer is about 0.6 grams/denier and above. The elongation of the polyurethane polymer is about 400% and above. All of the above properties are present in fibers prepared from said polyurethane polymer.

The high molecular weight polyurethane polymers contain “hard” segments and “soft” segments arranged in an orderly, non-random fashion. The “hard” segments are a product of the reaction between the second low molecular weight diol monomer and a diisocyanate. The “soft” segments are a product of the reaction between the first high molecular weight diol monomer and a diisocyanate monomer.

The melt spinnable composition containing the high molecular weight polyurethane polymer can be prepared by a process comprising the steps of: obtaining a polyol prepolymer which is a member selected from the group consisting of polyether diols, hydroxyl terminated polyester glycols, hydroxyl terminated polyether/polyester glycols, and mixtures thereof; adding to the polyol prepolymer a first organic diisocyanate to obtain a first mixture. The first mixture is then reacted under suitable reaction conditions to obtain a first polymer. This first polymer will become the “soft” segment in the final high molecular weight polyurethane polymer.

The process is then continued by obtaining a low molecular weight glycol; adding the glycol to a second organic diisocyanate to obtain a second mixture. The second mixture is then reacted under suitable reaction conditions to obtain a second polymer. The second polymer will become the “hard” segment in the final high molecular weight polyurethane polymer.

This second polymer typically has a molecular weight low enough to be metered to the [reactor] reaction extruder. Viscosity must be controlled to allow the second polymer to be combined with the first polymer in [a] the reaction extruder. This can be accomplished by reacting the low molecular weight diol with a suitable diisocyanate under conditions to maintain production of a second polymer of sufficiently low molecular weight.

To continue the process, the first polymer is combined with the second polymer in a reaction extruder under suitable reaction conditions. In a preferred embodiment, the mole ratio of isocyanate functionality to hydroxyl functionality in the combination of polymers is about 0.98:1 to about 1.2:1. A final product of high molecular weight polyurethane is withdrawn from the reaction extruder.

The process further comprises the steps of pelletizing the solid high molecular weight polyurethane, melting the pelletized material and then spinning the melted polyurethane into elastomer fibers.

In an alternative embodiment, the solid product withdrawn from the reaction extruder can be pelletized, melted, and then spun as a fiber into a vaporous [low molecular weight] aliphatic diamine. The fiber, as a result of this treatment, will have a minor amount of urea functionality.

In yet another alternative embodiment, the solid product withdrawn from the reaction extruder can be pelletized, melted, and then spun as a fiber into an aqueous solution of [low molecular weight] aliphatic diamine. Once again, the fiber will then have a minor amount of urea functionality.

In reference to the process step of adding a first organic diisocyanate to the polyol prepolymer, the mole ratio of isocyanate groups to hydroxyl groups in the mixture is preferably about [1.2] 2:1 to about 1:1.1. The mixture is then preferably heated at a temperature of about 60°C to about 100°C and at atmospheric pressure for a time of about 20 minutes to about 100 minutes.

In reference to the process step of adding a second organic diisocyanate to the low molecular weight glycol, the mole ratio of isocyanate groups to hydroxyl groups in the mixture is [preferable] preferably about 1:2 to about 1:1.2. The mixture is then preferably heated at a temperature of about 50°C to about 70°C and at atmospheric pressure for a time of about 2 minutes to about 10 minutes.

In reference to the process step of combining the first “soft” polymer with the second “hard” polymer in a reaction extruder, the two polymers are contacted in the reaction

extruder along with excess diisocyanate to obtain a ratio of free isocyanate groups to free hydroxyl groups of about 1:1 under high mixing conditions and a temperature of about 125°C to about 260°C for a time of about 2 minutes to about 8 minutes and at atmospheric pressure. The three-step process depends on the use of a controlled polymerization reaction to obtain a meltable form of the second polymer ("hard segment"), prepared from the low molecular weight diol and a second diisocyanate, for addition to the first polymer ("soft segment") in the reaction extruder. The final polyurethane polymer product can then be withdrawn from the reaction extruder, pelletized, melted, and spun into fibers.

The low molecular weight glycol preferably contains 2 to about 20 carbon atoms. Typical examples of such glycols include ethylene glycol, propylene glycol, 1, 6-hexane diol, 1, 4-butanediol, neopentyl glycol, diethylene glycol, thiodiglycol, 2, 2-dimethyl-1, 3-propylene glycol, and the like. In a most preferred example, the glycol is a C₂-C₆ glycol.

The polyol prepolymer preferably has a number average molecular weight of about 1000 and above, most preferably about 2000 to 6000. Such a prepolymer can be a chain extended polyester made from a glycol, preferably a mixture of ethylene and butylene glycols, and a saturated organic dicarboxylic acid, preferably adipic acid. The acid usually contains 4 to 20 carbon atoms. Typical examples include succinic acid, maleic acid, dihydromalonic acid, thiodipropionic acid, adipic acid, methyl adipic acid, glutaric acid, dimerized

linoleic acid, sebacic acid, suberic acid, phthalic acid, and terephthalic acid. To some extent hydroxycarboxylic acids or their lactones can be used, eg., caprolactone, to aid in forming the polyesters. As stated, mixtures of various dibasic acids and glycols can be used to form mixed esters.

An excess of the glycol over the acid is used in preparing the polyesters so that the resulting polyester contains terminal hydroxyl groups. In general, the most suitable polyesters are chiefly linear with melting point levels of 20°C or lower and preferably not over 30°C. Less suitably natural polyesters can be used, eg., castor oil, as well as blown drying oils such as blown tung oil, linseed oil and soya oil.

As an alternative to the polyesters there may be used for reaction with the diisocyanate one or more elastomer yielding polyethers. Such polyethers are typically anhydrous chain extended polyethers possessing ether linkage separated by hydrocarbon chains either alkyl or aryl in nature. The ether should also contain terminal groups reactive [to] with isocyanate, such as alcoholic hydroxyl groups. Such polyethers should be linear with a second order transition point of not over 25°C, preferably not over 10°C. The number average molecular weight range is from 500 – 7000, but preferably is within the range of 1000 to 5000. Preferred polyethers have the formula $H(OR)_nOH$ where R is a lower alkylene group (2 to 6 carbon atoms) and n is an integer so that the molecular weight falls within the range specified. Examples of polyethers are polyethylene glycol, polypropylene glycol, polybutylene glycol,

mixed polyethylene glycolpolypropylene glycol,
polytetramethylene glycol (e.g., of 1000 number average
molecular weight).

Polyethers not only can be used in place of the polyesters
but can be used in conjunction therewith. Examples of such
compounds are polydiethylene glycol adipate. Further
examples of polyesters and polyethers which are suitable are set
forth in Kohn Patent 2,953,839 and the patents cited therein
(column 2, lines 56-68).

Long lengths of "soft" segments are desired. In the fiber
prepared from the final polyurethane elastomeric product, the
"soft" segments regulate the elongation of the fiber and the
recovery from stretch of the fiber. In order to obtain long
lengths of "soft" segments, higher molecular weight diols can
be employed. Another approach to achieving long lengths of
"soft" segments is to regulate the capping ratio[so that the mole
ratio of isocyanate to hydroxyl is in the range of about 1:2 to
about 1:1.1]. This cannot be done in the "one shot" process.

The "soft" segments are oligomeric or polymeric and
comprise blocks of polymeric glycol (poly)urethanes end
capped with isocyanate groups. The "hard" segments are
oligomeric or polymeric and comprise blocks of low molecular
weight C₂ –C₆ glycol (poly)urethanes having free hydroxyl end
groups. Both the "soft" segments and the "hard" segments are
structured so that they can chemically interact with one another
under suitable polymerization conditions to obtain a final TPU
(thermoplastic urethane) polymer.

Representative of the preferred aromatic diisocyanates which may be mentioned, by way of non-limiting examples are m- and p-phenylene diisocyanate, tolylene diisocyanate (65% 2, 4 and 35% 2, 6), p,p' - diphenylisocyanate, 1, 5 naphthalene diisocyanate, p, p'-diphenyl-methane diisocyanate, 3, 3'-bitolylene-4, 4'-diisocyanate, 2, 4-tolylene diisocyanate dimer, dianisidine diisocyanate, 4-chloro-1, 3-phenylene diisocyanate. Aliphatic and cycloaliphatic diisocyanates can also be used, such as 1, 4-tetramethylene diisocyanate, 4, 4'-methylene-bis (cyclohexylisocyanate), and 1, 5-tetrahydronaphthalene diisocyanate. Other diisocyanates can be employed including those set forth in the Kohn Patent, as well as those mentioned in the patents set forth in Kohn. The preferred diisocyanate is tolylene diisocyanate.

The vaporous [low molecular weight] aliphatic diamine generally has the formula $H_2N-A-NH_2$, where A is a divalent organic radical in which the terminal atoms are carbon, and which is devoid of groups reactive with isocyanate. As suitable amines there can be used ethylene diamine, hexamethylene diamine, 1, 4-diaminocyclohexane, p-phenylenediamine, 3-3'-diaminodipropyl ether, diaminodibutyl sulfide, propylene diamine. The preferred diamine is ethylene diamine.

Preferably, catalysts are employed in the final step of the three-step process to obtain a final polyurethane elastomeric product. Examples of catalysts are triethylamine, cobalt naphthenate, stannous chloride, tetra-n-butyl tin, stannic chloride, tri-n-butyl tin acetate, n-butyl tin trichloride, trimethyl

tin hydroxide, dimethyl tin dichloride, and di-n-butyl tin dilaurate. Because of the short residence time of the reactants in the reaction extruder during the final step of the three-step process, and also because of the relatively small volume inside the extruder, catalysts are usually necessary in order to speed the reaction and obtain high molecular weight thermoplastic polyurethanes. An extruder of relatively low volume is required to allow for good mixing conditions under standard power requirements.

Any conventional extruder can be employed in the process of preparing the final polyurethane elastomer product. The reaction extruder preferably employs a twin-screw, co-rotating, self-wiping, multi-heating zone design. In a preferred embodiment, the extruder has a length to diameter ratio of about 46:1 and greater. The free volume in the extruder should allow for a residence time of about 2 minutes to about 8 minutes. Extruders made by Bersdorff or Davis Standard are acceptable for use.

The ratio of the reactants, the temperature of the reaction, and the time of the reaction are all critical factors in determining the length of the first "soft" segment, which ultimately regulates the elongation and recovery properties of the fiber. The length of the first "soft" segment can be in multiples of the starting polyol; so that if the starting polyol has a number average molecular weight of about 2000, then the length of the "soft" segment, when prepared under proper conditions, can contain some segments from 10,000 to even

about 40,000 molecular weight. [The proper conditions include an isocyanate to hydroxyl ratio of 1:2 to about 1:1.1. "Soft" segments having molecular weights which are multiples of the molecular weight of the starting polyol can be formed when the isocyanate to hydroxyl ratio is less than about 1:2. This is because some of the molecules have one end with an isocyanate group and one end with a hydroxyl group, making them self-reactive.]

In an alternative embodiment, a thermoplastic polyurethane elastomeric polymer having sufficient lengths of "soft" segments can be prepared from a two-step process. An adequate alignment of "soft" segments and "hard" segments is obtained in the final polymer. In a first step, a prepolymer is formed from a diisocyanate and polyether diol, a polyester diol, a mixed polyether-polyester diol or mixtures thereof. This prepolymer has "soft" segments of a diol end capped with diisocyanate groups. The first step is performed with good mixing and in a time of about 20 minutes.

In this alternative embodiment, only one prepolymer is prepared, and that prepolymer is the "soft" segment. The second step requires the addition of the prepolymer to a reaction extruder along with more diisocyanate and a low molecular weight glycol. Preferably, a catalyst is also added to the mixture in the reaction extruder. Catalysts can be selected from the group listed above in the disclosure of the three-step process. The reaction in the extruder includes both the "in situ" formation of "hard" segments and the formation of the final

thermoplastic polyurethane elastomer having well-defined blocks of “soft” segments and random blocks of “hard” segments. The compounds added to the reaction extruder in the two-step process are adjusted in amount so that the mole ratio of isocyanate to hydroxyl approaches 1.000, with the proviso that gel formation should be avoided. The temperature of the reaction extruder should be controlled within the range of about 200°C to about 250°C.

In a modification of the two-step process, all of the diisocyanate necessary for formation of both the “soft” segment and “hard” segment can be added at once, during the first step. The product mixture obtained after the first step contains a first polymer (“soft segment”) and unreacted diisocyanate. The product mixture from the first step is added to a reaction extruder in a second step along with a low molecular weight glycol. Optionally, a catalyst can also be added to the extruder. Under appropriate reaction conditions, the second polymer (“hard segment”) is formed “in situ” and then a final thermoplastic polyurethane (TPU) elastomer is formed.

Fibers prepared from the TPU (thermoplastic urethane) elastomeric compositions of the two-step process do not have physical properties identical to the fibers prepared from polymeric compositions prepared according to the three-step process. However, the physical properties of both the “two-step process” fibers and the “three-step process” fibers are adequate for the manufacture of textile materials and the like. The two-

step process requires less equipment and less control than the three-step process.

In both the two-step process and the three-step process, the physical properties of the fibers are dependent on the following parameters: (1) the ratio of “hard” segments in the polymer backbone; (2) the uniformity of the distribution of blocks of “hard” segments and blocks of “soft” segments in the polymeric backbone; (3) the length of the “soft” segment in the polymeric backbone; and (4) the post-treatment regimen (e.g., stretching, heat setting, and the like conducted on the fiber).

All the parameters disclosed above are to be considered when a manufacturer produces a TPU elastomeric polymer composition suitable for melt spinning into fibers useful in the textile industry. Any of the parameters can be varied within certain ranges in the interest of economics and still obtain useful fibers.

The multi-step processes disclosed above have many advantages over the prior art processes as presented in the literature. Both multi-step processes disclosed above yield a melt spinnable polymeric material. There is no need or limited need for the use of solvents, and therefore the processes are environmentally friendly. The polymers prepared according to the multi-step processes herein disclosed have a combination of high tenacity, high recovery from stretch, high elongation and freedom from any gels greater than 20 micrometers.

All prior art one-shot processes cannot produce the necessary alignment of “soft” segments and “hard” segments.

A one-shot process is when all reagents (polyol, glycol, diisocyanate and catalyst) are metered simultaneously into a reaction extruder. The products are polyurethanes from polymeric glycols and low molecular weight glycols, said products having random distributions of urethane linkages in the polymeric backbone. There is no adequate alignment of “soft” segments and “hard” segments, as all reactions in the extruder are completed in a random fashion and usually in less than three minutes. When such a situation exists, small amounts of materials reach a molar ratio of isocyanate to hydroxyl of exactly 1.000. When such a ratio is reached, a polymer of “infinite” molecular weight is formed (gels). It is practically impossible to prevent such a situation when a one-shot process is employed.

One-shot processes are usually conducted at a temperature of about 125°C to about 260°C and at a time of about 3 minutes. Only one reaction extruder is employed, and no prepolymers are formed (except for the uncapped polyol). The final TPU elastomeric product contains only random alignments of “hard” segments and “soft” segments. The one-shot processes lack the ability to precisely control the desired high molecular weights.

In the multi-step processes herein disclosed, choice of catalyst greatly affects the reaction rate of the isocyanate and hydroxyl group. For example, if an uncatalyzed reaction of isocyanate with hydroxyl group is designated as having a reaction rate of 1, then the reaction rates of isocyanate with

hydroxyl group for various catalysts are as follows:

triethylamine (11), cobalt naphthenate (23), stannous chloride (68), tetra-n-butyl tin (82), stannic chloride (99), tri-n-butyl tin acetate (500), n-butyltin trichloride (83), trimethyl tin hydroxide (1800), dimethyltin dichloride (2100), and di-n-butyl tin dilaurate (37000). Also, undesirable side reactions of the isocyanate with water are suppressed by the use of a catalyst. With the use of dibutyltin diacetate, the rate of reaction of isocyanate with hydroxyl group as compared to the reaction of isocyanate with water is about 6:1.

While the invention has been described by specific embodiments, there is no intent to limit the inventive concept except as set forth in the following claims.



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Claims

We Claim:

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- 1) (Amended) A [melt spinnable] composition useful in preparing melt spun textile fibers comprising a [high molecular weight] polyurethane polymer prepared from at least one diisocyanate monomer and at least two diol monomers, a first diol monomer [of relatively high molecular weight] having a number average molecular weight of about 1,000 to about 8,000 and a second diol monomer [of low] having a molecular weight of about 62 to about 118, said polyurethane having a number average molecular weight [above] of about 200,000 and above, a tenacity [above] of about 0.6 gm/denier and above, and an elongation [above] of about 400% and above, wherein said first and second diol monomers are always reacted separately during preparation of the polyurethane polymer.

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- 2) (Cancelled) [A composition according to claim 1 wherein the second low molecular weight diol has a molecular weight of about 62 to about 118.]

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- 3) (Cancelled) [A composition according to claim 1 wherein the first relatively high molecular weight diol has a molecular weight of about 1000 to about 8000.]

- 5 4) (Original) A composition according to claim 1 wherein the first diol monomer is a member selected from the group consisting of a polyether diol, a polyester diol and a mixed polyether-polyester diol.
- 10 5) (Amended) A composition according to claim 1 wherein the at least one diisocyanate monomer is a member selected from the group consisting of aliphatic monomers having terminal isocyanate groups, aromatic monomers having terminal isocyanate groups, mixtures of said aliphatic and aromatic monomers [and, isomeric mixtures of said aliphatic or aromatic monomers.] , mixtures of isomers of an aliphatic monomer having terminal isocyanate groups and mixtures of isomers of an aromatic monomer having terminal isocyanate groups.
- 15 6) (Original) A composition according to claim 5 wherein the at least one diisocyanate monomer is a member selected from the group consisting of 1, 6-hexane diisocyanate, toluene diisocyanate isomers and methylene bis (phenylisocyanate) isomers.
- 20 7) (Amended) A composition according to claim 1 wherein the [high molecular weight] polyurethane polymer contains “hard” segments and “soft” segments, said
- 25

segments arranged in an orderly[, non-random] fashion[
to obtain discrete distances between urethane groups].

5 8) (Amended) A composition according to claim 1 wherein
the [high molecular weight] polyurethane polymer
contains [a small amount of urea groups wherein said
urea groups are] urea functionality obtained by post-
treatment of the polyurethane polymer with a [low
molecular weight] diamine[.] which is a member selected
10 from the group consisting of ethylene diamine;
hexamethylene diamine; 1, 4-diaminocyclohexane; p-
phenylenediamine; 3, 3'-diaminodipropyl ether;
diaminodibutylsulfide; and propylene diamine.

15 9) (Amended) A composition according to claim 8 wherein
the [low molecular weight] diamine comprises ethylene
diamine.

20 10) (Amended) A process of preparing a polyurethane
polymer fiber precursor, the process comprising the steps
of:

a) obtaining a polyol prepolymer which is a
member selected from the group consisting of
hydroxyl terminated polyester glycols,
25 hydroxyl terminated polyether glycols,
hydroxyl terminated polyether/polyester
glycols, and mixtures thereof;

- 5 b) adding a first organic diisocyanate to the polyol prepolymer wherein the mole ratio of isocyanate group to hydroxy group [diisocyanate to prepolymer] is about [1.2] 2:1 to 1:1.1 to obtain a first mixture;
- 10 c) reacting the first mixture of first organic diisocyanate and polyol prepolymer at a temperature of about 60°C to about 100°C and at atmospheric pressure for a time of about 20 minutes to about 100 minutes to obtain a [first] “soft” polymer [having a viscosity of about 50-800 poises];
- 15 d) obtaining a [low molecular weight] glycol having terminal hydroxyl groups;
- e) adding a second organic diisocyanate to the glycol wherein the mole ratio of isocyanate to hydroxyl is about [1.2] 1:2 to about 1:1.2 to obtain a second mixture;
- 20 f) reacting the second mixture of second organic diisocyanate and [low molecular weight] glycol at a temperature of about 50°C to about 70°C and at atmospheric pressure for a time of about 2 minutes to about 10 minutes to obtain a [second] “hard” polymer;
- 25 g) combining the [first] “soft” polymer from (c) with the [second] “hard” polymer from (f) in an extruder to obtain a combination of polymers

wherein the mole ratio of isocyanate
functionality to hydroxyl functionality in the
combination is about 0.98:1 to about 1.2:1;

h) reacting the combination of polymers in the
extruder under [polymerization and high
mixing] suitable reaction conditions and at a
temperature of about 125°C to about 260°C for
a time of about 2 minutes to about 8 minutes
and at atmospheric pressure to obtain a final
polyurethane polymer; and

j) extruding the final polyurethane polymer to
obtain a solid product of polyurethane polymer
fiber precursor.

11) (Amended) A process according to claim 10 further
comprising the steps of:

k) pelletizing the solid product of polyurethane
polymer fiber precursor;

l) melting the pelletized solid product; and

m) spinning the melted product to obtain a
[Spandex-like] polyurethane polymer fiber.

12) (Amended) A [Spandex-like] polyurethane polymer fiber
prepared according to the process of claim 11.

13) (Amended) A process according to claim 10 further
comprising the steps of:

(k') pelletizing the solid product of polyurethane polymer fiber precursor;
(l') melting the pelletized solid product; and
(m') spinning the melted product in the presence of
a [low molecular weight aliphatic] diamine vapor
which diamine is a member selected from the
group consisting of ethylene diamine;
hexamethylene diamine; 1, 4-diaminocyclohexane;
p-phenylenediamine; 3, 3'-diaminodipropyl ether;
diaminodibutylsulfide; and propylene diamine; to
obtain a [Spandex-like] polyurethane polymer
fiber which contains [having a minor amount of]
urea functionality.

14) (Amended) A [Spandex-like] polyurethane polymer fiber
[having a minor amount of] which contains urea
functionality prepared according to the process of claim
13.

15) (Amended) A process according to claim 10 further
comprising the steps of:

(k'') pelletizing the solid product of polyurethane
polymer fiber precursor;
(l'') melting the pelletized solid product; and
(m'') spinning the melted product into an aqueous
solution of [low molecular weight aliphatic]
diamine which diamine is a member selected from

the group consisting of ethylene diamine;
hexamethylenediamine; 1, 4-diaminocyclohexane;
p-phenylenediamine; 3, 3'-diaminopropyl ether;
diaminodibutylsulfide; and propylene diamine; to
5 obtain a [Spandex-like] polyurethane polymer
fiber [having a minor amount of] which contains
urea functionality.

10 16) (Amended) A [Spandex-like] polyurethane polymer fiber
[having a minor amount of] which contains urea
functionality prepared according to the process of claim
15.

15 17) (Original) A process according to claim 10 wherein the
polyol prepolymer of step (a) is a liquid under standard
conditions of temperature and pressure.

20 18) (Original) A process according to claim 10 wherein the
first organic diisocyanate of step (b) and the second
diisocyanate of step (e) are each a member selected from
the group consisting of 1, 6-hexane diisocyanate, toluene
diisocyanate isomers, and methylene bis
(phenylisocyanate) isomers.

25 19) (Original) A process according to claim 10 wherein step
(h) is conducted in the presence of a catalyst.

20)(Amended) A process for preparing a polyurethane polymer fiber precursor, the process comprising the steps of:

(a) obtaining a polyol prepolymer which is a member selected from the group consisting of hydroxyl terminated polyester glycols, hydroxyl terminated polyether glycols, hydroxyl terminated polyether/polyester glycols, and mixtures thereof;

(b) adding [an] a first organic diisocyanate to the polyol prepolymer wherein the mole ratio of isocyanate to hydroxyl is about [1:2] 2:1 to about 1:1.1 to obtain a first mixture;

(c) reacting [a] the first mixture of first organic diisocyanate and polyol prepolymer at a temperature of about 60°C to about 100°C and at atmospheric pressure for a time of about 20 minutes to about 100 minutes to obtain a [first] “soft” polymer [and unreacted diisocyanate];

(d) obtaining a [low molecular weight] glycol having terminal hydroxyl groups;

(e) [adding the first polymer and the unreacted diisocyanate from step (c) to the low molecular weight glycol in a reaction extruder to obtain a second mixture wherein the mole ratio of isocyanate group to hydroxyl group approaches 1.000;]obtaining a second organic diisocyanate;

(f) [reacting the second mixture of first “soft” polymer, unreacted diisocyanate and low molecular weight glycol in the reaction extruder under polymerization and high mixing conditions and at a temperature of about 125°C to about 260°C. for a time of about 2 minutes to about 8 minutes and

at atmospheric pressure to obtain a final polyurethane polymer; and] combining the “soft” polymer with the glycol of step (d) and the second organic diisocyanate of step (e) in a reaction extruder to obtain a combination of “soft”

5 polymer, glycol and diisocyanate, wherein the mole ratio of isocyanate group to hydroxyl group is adjusted to approach 1:1, with the proviso that gel formation is avoided;

(g) [extruding the final polyurethane polymer to obtain a solid product of polyurethane polymer fiber precursor.]

10 reacting the combination of “soft” polymer, glycol and diisocyanate in the reaction extruder under suitable reaction conditions and at a temperature of about 125°C to about 260°C for a time of about 2 minutes to about 8 minutes and at atmospheric pressure to obtain a final polyurethane polymer; and

15 (h) extruding the final polyurethane polymer to obtain a solid product of poly urethane polymer fiber precursor.

21)(Amended) A process according to claim 20 further comprising the steps of:

20 ([h] l) pelletizing the solid product of polyurethane polymer fiber precursor;

([j] k) melting the pelletized solid product; and

25 ([k] l) spinning the melted product to obtain a [Spandex-like] polyurethane polymer fiber.

22) (Amended) A [Spandex-like] polyurethane polymer fiber prepared according to the process of claim 21.

23) (Amended) A process according to claim 20 further comprising the steps of:

5 ([h'] j') pelletizing the solid product of polyurethane polymer fiber precursor;

([j'] k') melting the pelletized solid product; and

10 ([k'] l') spinning the melted product in the presence of a [low molecular weight aliphatic] diamine vapor which is

a member selected from the group consisting of ethylene diamine; hexamethylene diamine; 1, 4-

diaminocyclohexane; p-phenylenediamine; 3, 3'-

diaminopropyl ether; diaminodibutyl sulfide; and

15 propylene diamine; to obtain a [Spandex-like]

polyurethane polymer fiber [having a minor amount of] which contains urea functionality.

24) (Amended) A [Spandex-like] polyurethane polymer fiber [having a minor amount of] which contains urea functionality prepared according to the process of claim 23.

25) (Amended) A process according to claim 20 further comprising the steps of:

25 ([h''] j'') pelletizing the solid product of polyurethane polymer fiber precursor;

5 ([j"] k") melting the pelletized solid product; and
([k"] l") spinning the melted product into an aqueous
solution of [low molecular weight aliphatic] a diamine
which is a member selected from the group consisting of
ethylene diamine; hexamethylene diamine; 1, 4-
diaminocyclohexane; p-phenylenediamine; 3, 3'-diamino
propyl ether; diaminodibutyl sulfide; and propylene
diamine; to obtain a [Spandex-like] polyurethane
polymer fiber [having a minor amount of] which contains
10 urea functionality.

15 26) (Amended) A [Spandex-like] polyurethane polymer fiber
[having a minor amount of] which contains urea
functionality prepared according to the process of claim
25.

20 27) (Original) A process according to claim 20 wherein the
organic diisocyanate of step (b) is a liquid under standard
conditions of temperature and pressure.

25 28) (Original) A process according to claim 20 wherein the
organic diisocyanate of step (b) is a member selected
from the group consisting of 1, 6-hexane diisocyanate,
toluene diisocyanate isomers, and methylene bis
(phenylisocyanate) isomers.

- 29) (Amended) A process according to claim 20 wherein step [(f)] (g) is conducted in the presence of a catalyst.